

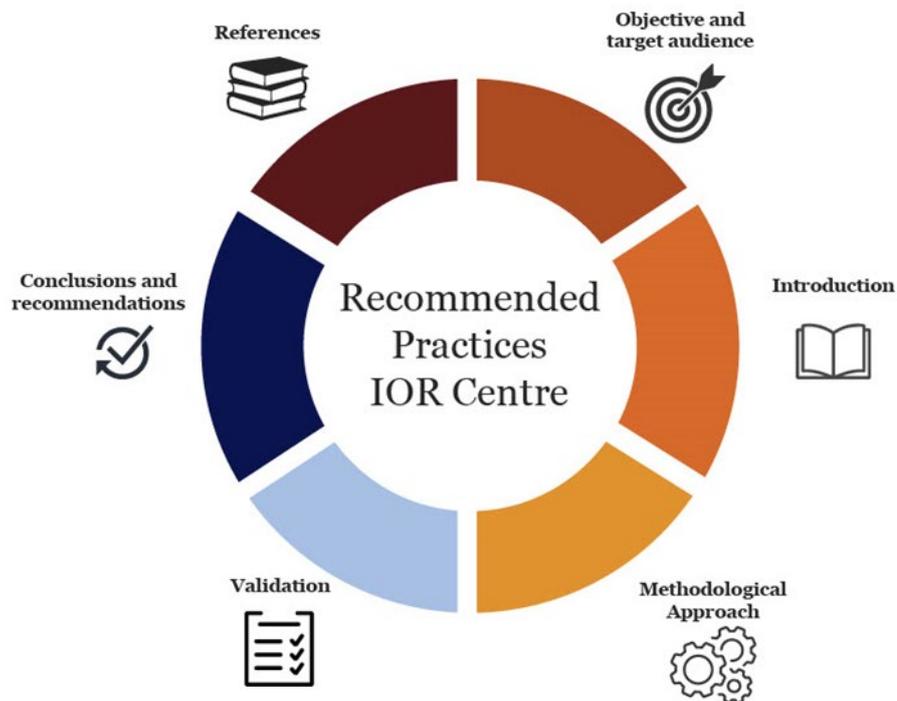
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Lanthanide-Complexed Esters for Single-Well SOR Measurements

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Objective and target audience	2
Introduction	2
Methodological Approach	4
Wanted complexation agent properties	4
Synthesis	5
Separation and analysis	6
Fluorescence lifetime:	7
Hydrolysis rate	7
Water/oil partitioning.....	7
Validation	8
Conclusions and recommendations	8
Future work.....	8
Spin-off.....	9
References	9

Objective and target audience

The main objective has been to improve the prevailing single-well chemical tracer push-and-pull technique, SWCTT, for measurement of residual oil saturation (SOR) in defined pay zones in a single well test [1,2,3] after water injection on the following subjects:

- Improvement in tracer detection limits by a factor > 1000
- On-site or even on-line detection of tracer signal in true time
- Reduction in the needed amount of tracer by a factor of > 1000
- Reduced footprint on production platforms during tracer operation

The intended audience and technology users are oil and service companies.

Introduction

The prevailing technique for measurement of SOR after water injection in a single well tracer test consists of the following operational points:

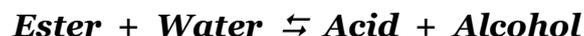
1. **Injection:** Inject a water-based ester solution as a pulse out to some 5-10 m from the well (as a doughnut). The ester is water/oil partitioning, and governed by a partition constant K which is a function of pH, temperature, water salinity, molecular content of residual oil etc.:

$$K = \frac{\text{Concentration of ester in the oil phase at partition equilibrium}}{\text{Concentration of ester in the water phase at partition equilibrium}} = \frac{[Tr]_{o,eq}}{[Tr]_{w,eq}}$$

Here, Tr is the symbol of the ester tracer.

If the experimental conditions are constant, the K -value is constant. Oil partitioning of the ester means that the movement of the ester is lower than the water itself because the partition equilibrium demands that some ester, at any time, to be present in the stagnant residual oil. The most used esters today are ethyl- and propyl-esters.

2. **Well shut-in:** The injection is stopped, and the well is shut in for 2-4 days (mainly depending on temperature and type of ester) in order for the ester to hydrolyze, i.e. react with the surrounding water. This reaction is continued until approximately 50 % of the ester is estimated to be hydrolyzed. The hydrolysis reaction is proceeding according to the chemical reaction below:



3. **Back-production:** After the shut-in period the back-production of the remaining ester and the produced alcohol (and acid) starts. The alcohol is a pure and passive water tracer and does not partition into oil. The volumetric distribution of the alcohol at the end of the shut-in period is, ideally, identical to the distribution of the remaining (ca. 50%) ester, i.e. on back-production they “start on the same starting line”. Thus, on back-production, the alcohol follows passively the water phase while the remaining ester will partition into the water-contactable residual oil and be delayed with respect to the water flow.
4. **Sampling/analysis:** The back-produced water is sampled frequently as a function of time, and the concentration of ester and alcohol in each sample is analysed largely by

gas chromatography (GC). Most of the time, samples are shipped from the production site to a laboratory situated elsewhere for analysis. Establishment of tracer production curves is performed based on analytical results.

5. Result interpretation: Interpretation of the tracer production curves can take different routes. The most correct procedure is probably to establish the *first moments* of the distributions of the two recorded production curves. The distance between the times represented by the first moments (or alternatively produced water volumes for the first moments, see Figure 1 below) of the two distributions is proportional to the water-contactable SOR.

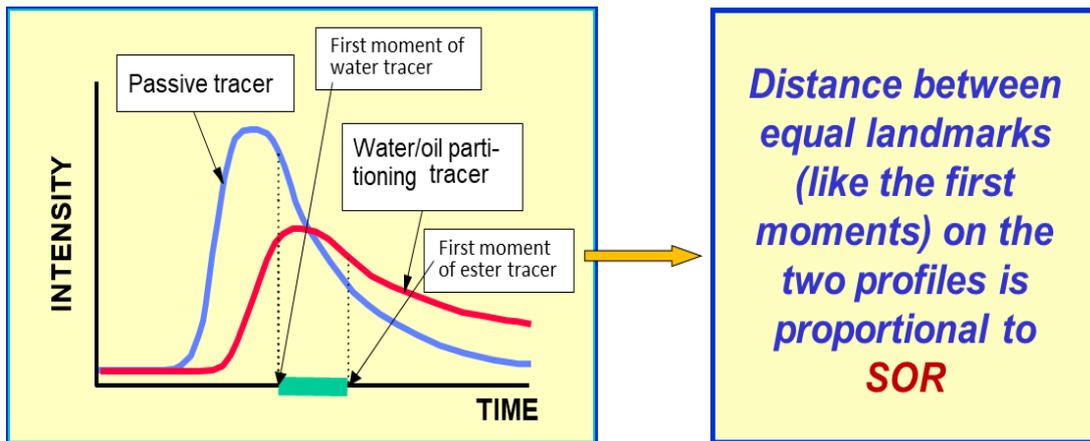


Fig.1. Principle illustration of back-produced passive tracer (produced alcohol) and water-oil partitioning tracer (remaining ester) and the distance between their first moments which is proportional to water-contactable remaining oil saturation.

Problem areas which may obstruct the results from ideality (not further treated in this project):

- Fluid drift in the reservoir during shut-in: This point is normally taken care of by injection of a so-called cover tracer throughout the injection period.
- Hydrolysis of the ester also during injection and back-production: Must be corrected for by modelling.

Improvement areas addressed in this project:

- New esters with different analytical expression: Development of new esters based on lanthanide complexes is in focus for extensively improved lower detection limit (LOD) where the detection principle is based on laser- (or light-) induced *fluorescence*. The fluorescence is caused by the lanthanide ion present, and it is specific and strong (selective and sensitive).
- On-line analysis: This fluorescence method offers possibility for on-site or even on-line continuous analysis of back-produced tracer compounds.
- Effective removal of acid catalysis rate problem on the hydrolysis: Ester hydrolysis rate is catalyzed by both acid and base. The lowest rate is in the range pH 6-7. The acid produced during hydrolysis may continuously modify the hydrolysis rate if injected amount of tracer is high (as in the case of ethyl- and propyl esters) and if the buffering capacity of the surrounding water and rock is low. Reduction in tracer amount by a factor of > 1000 may effectively remove this problem.

- Modification of near-well formation properties: Any potential modification of chemical properties in the near-well probed volume due to injection of massive amount of tracer (read: ester) is removed due to low tracer amount.
- Accuracy: Thus, the sensitivity and accuracy of the method is expected to improve.
- Environmental impact and footprint: The low amount of tracer (a few hundred grams) leads to much lower potential environmental impact, to easier logistics and to a reduced space requirement (footprint) on the production platform.

The content of this project is inspired by our experience from conducting single-well SOR-measurement operations on the Norwegian Continental shelf.

Methodological Approach

Wanted complexation agent properties

Due to their unique electronic configuration ($[Xe]4fn$), the trivalent ions of the lanthanides (Ln^{3+}) display long-lived and narrow-line fluorescence emission bands in the UV-visible region under UV excitation [4, 5], see Figure 2. The fluorescence is element-specific and strong. It is therefore of interest to examine the possibility to utilize this strong and unique fluorescence for analytical purposes. This requires the development of an ester with a lanthanide atom incorporated as a complex.

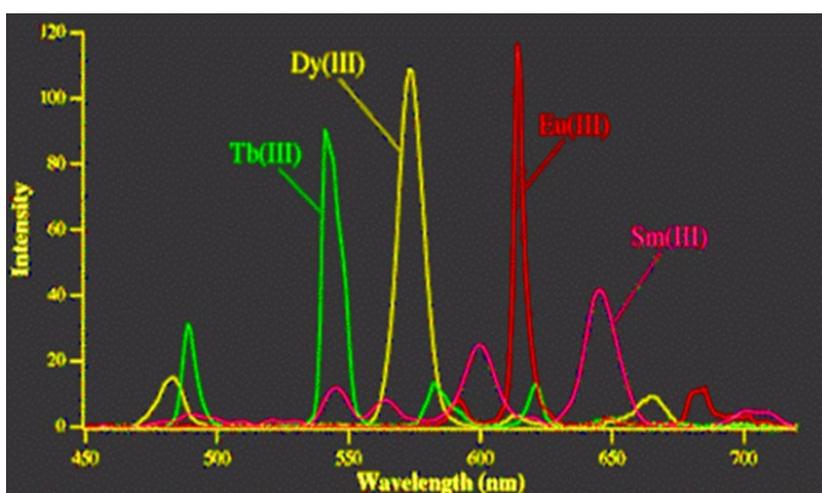


Fig.2. Example of fluorescence spectra of the lanthanides Tb, Dy, Eu and Sm.

Several molecular complexing agents for lanthanides were evaluated, all of which should exhibit the following properties:

- Form strong and thermally stable complex with Ln^{3+}
- Contain at least one carboxylic acid group to enable esterification with a selected alcohol
- Show molecular charge neutrality and bipolarity of the Ln^{3+} -complex
- Enable separation and detection by combining HPLC (or UPLC) with time-resolved fluorescence detection

- Show relatively long-lived fluorescence (phosphorescence) on the scale of milliseconds to enable discrimination of short-lived fluorescence from various water-soluble oil components.

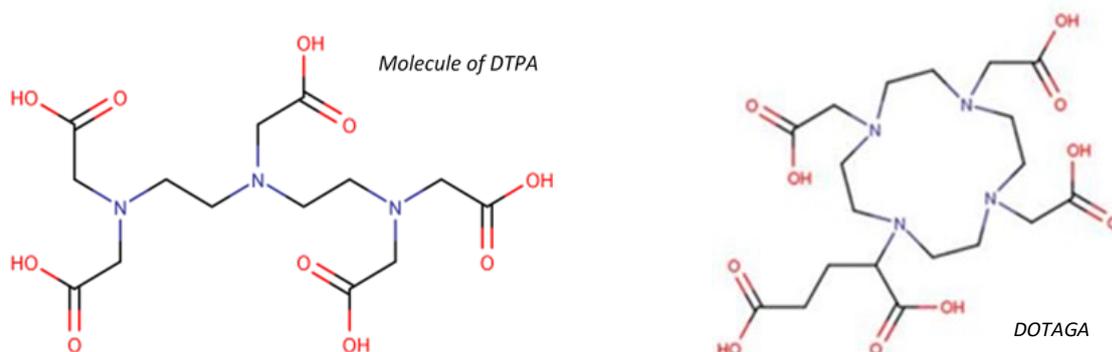


Fig. 3. Molecular configurations of the lanthanide complexing agents DTPA and DOTAGA

Synthesis

Two of the molecular complexing agents considered, DTPA and DOTAGA, are pictured in the Figure 3 above. Esterification of Ln-DTPA resulted, not unexpectedly, in a multi-ester complex that proved difficult to use at a later stage due to a complex pattern of hydrolysis. The desired molecular complex should, ideally, contain only one ester group. Hence, DOTAGA was selected as one of the most promising complexing agent candidates. This molecule has one of the five carboxylic acid groups in the end of a longer hydrocarbon chain. The esterification is expected to take place mainly at that position, and a monoester should be possible to obtain as a major reaction product.

Esterification was finally carried out in either DMSO or alcohol solution. Water could not be used because of hydrolysis.

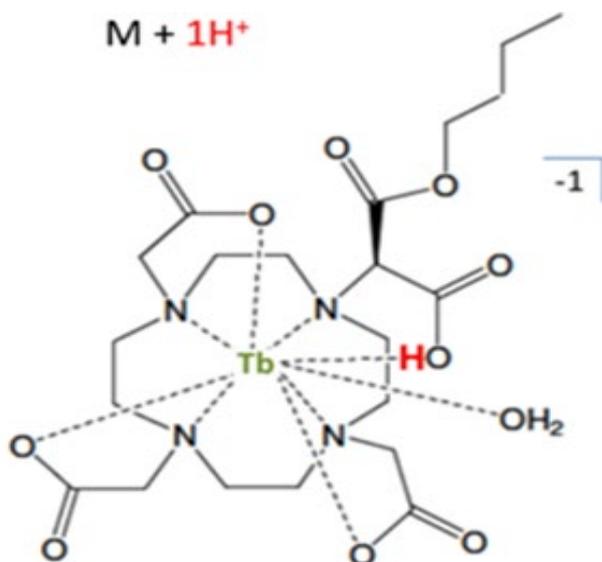


Fig.4. Monobutyl ester of the Tb-complex of DOTAGA

The Ln^{3+} complexation could be performed both before and after the esterification process to create DOTAGA-monoethyl- (or monobutyl-) ester-Ln complex, - the preferred method being complexation before esterification. The argument is that in this case, three of the carboxylic groups would bind to the central Ln^{3+} -ion, thus neutralizing the positive charge. Hence, these groups will be less available for esterification. Various reaction products were created, but they could be separated by HPLC/UPLC techniques. The configuration of one of the most interesting molecules is given in Figure 4 to the left which is the DOTAGA-monoethyl-ester-Tb complex.

All further details about the synthesis and molecular separation techniques are given in two technical reports [6,7].

Separation and analysis

Analytical methods based on HPLC/UPLC combined with mass spectrometry (MS) and time-resolved fluorescence (TRF) were developed for characterization of the products of the synthesis.

Figure 5 shows an ion chromatogram of the molecule pictured in Figure 4 while Figure 6 shows examples of HPLC-separation analyzed/detected with TRF.

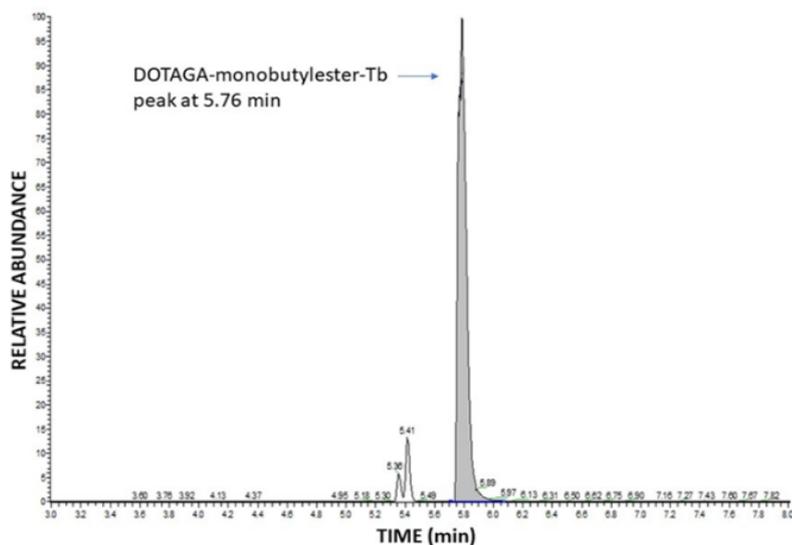


Fig.5. Extracted ion chromatogram of the DOTAGA-monoethyl-ester-Tb for a $m/z=689.1769-689.1925$ (form with three acidic groups complexing the terbium atom and one protonated acidic group).

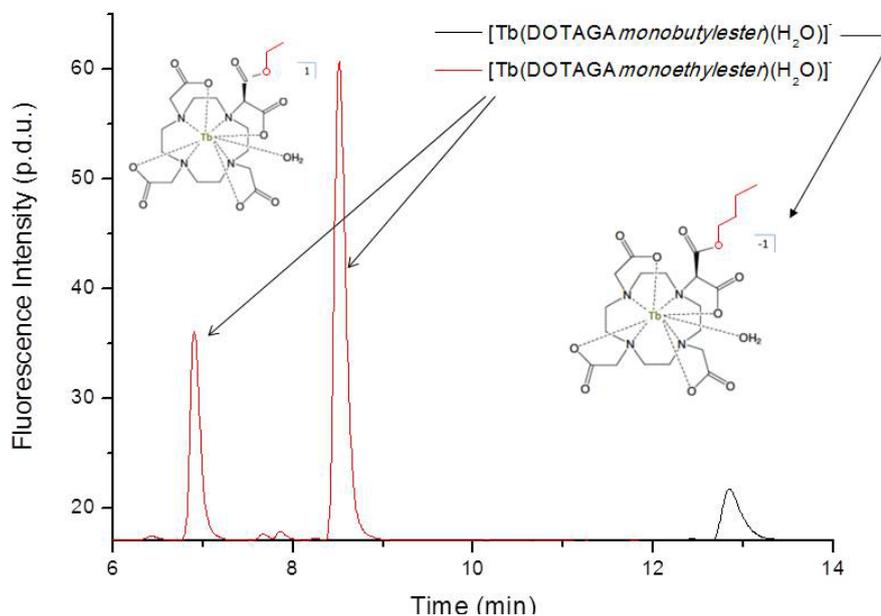


Fig.6. Examples of HPLC-separation analyzed/detected with time-resolved fluorescence (TRF).

Fluorescence lifetime:

Measurements of fluorescence lifetime showed that the DOTAGA-monoethyl-ester-Tb complex displayed a lifetime of 2.2 ms in DMSO. The lifetime increased to 2.7 ms with temperature treatment from 25-70 °C, indicative of formation of an even stronger complex. This lifetime is very suitable for TRF to discriminate against water-soluble oil components with fast lifetimes.

Hydrolysis rate

Hydrolysis rate was measured at the three different temperatures 50, 70 and 100 °C. Results are shown in Figure 7.

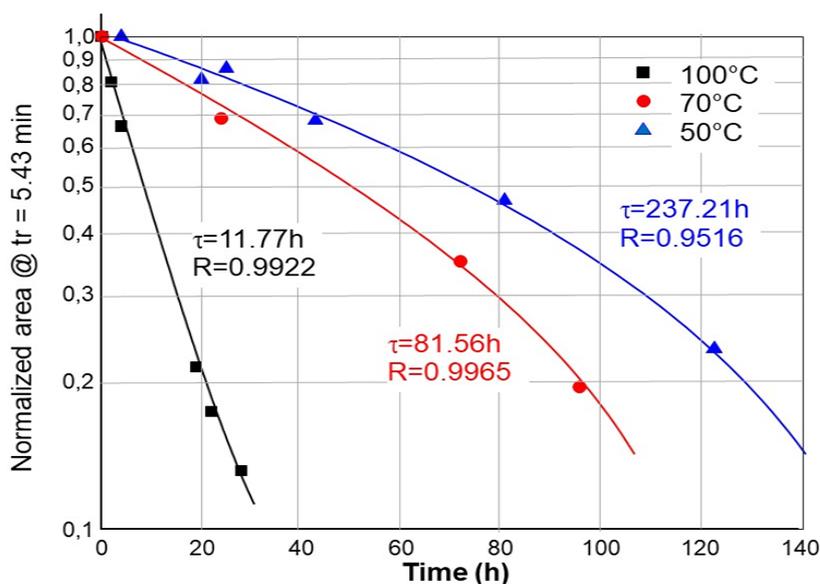


Fig.7. Hydrolysis rate: Diagram representing the absolute area of a strong elution peak (relative to the DOTAGA-monobutylester-Tb concentration) as function of time for three temperatures 50, 70 and 100°C.

The hydrolysis half-lives at 50, 70 and 100 °C were 9.8, 3.4 and 0.5 days, respectively, for the DOTAGA monobutylester-Tb.

These rates are suitable for SWCTT.

Water/oil partitioning

A desired value of the partition coefficient would be approximately $K \approx 3-6$.

500 μL of aqueous solution containing the tracer are vigorously shaken with 500 μL of the desired organic phase: crude oil (Norne oil), model oil and octanol. The pH was kept at ~7. The separatory vial is kept open at ambient temperature 10 minutes before 5 minutes centrifugation at 3000 rpm. 200μL of the aqueous phase are sampled and analyzed by HPLC-UV/Fluorescence or LC-MS. Conditions and results are summarized in Table 1.

Table 1: Conditions for partition tests

Waters	NORNE oil	Model oil 1	Model oil 2	Octanol
MilliQ W	No partitioning	No partitioning	No partitioning	No partitioning
Gullfaks W	No partitioning	No partitioning	No partitioning	No partitioning
1 g/L NaCl	No partitioning	No partitioning	No partitioning	No partitioning

The results have shown that this tracer is exclusively hydrophilic despite the attempt of increasing its affinity to the oil phase by esterification. The salinity and composition of the oil phase seems to have no influence on the partitioning for this compound.

The explanation is probably that the 4th carboxylic group was not protonated at the conditions of the experiment. Thus, the ester molecule would have an electric charge of 1-. Such a charged molecule will not partition into an oleic phase. This charge must be neutralized.

Accordingly, results suggest that this project has not yet reached its final goal because an ester with sufficiently phase-partitioning properties was not produced.

Validation

Due to the negative results in the final phase partitioning tests, there is, so far, no validation to be done. Otherwise, the ester would have been subject to dynamic laboratory experiments simulating the near-well formation with known oil saturation. Further, one would seek possibility of performing a push-and-pull test in a suitable field pilot project. These types of experiments will have to await a positive outcome of possible future experiments with respect to the phase-partitioning behavior.

Conclusions and recommendations

The outcome/results of all the defined tasks and work packages were positive except the last crucial one which deals with sufficient water/oil partitioning. Hence, at the present stage, the technology as such is not ready for field implementation.

Future work

What is needed is to mask or neutralize the negative charge (1-) of the ester on order to make the molecule more lipophilic. There are, perhaps, two ways to meet this challenge:

1. Apply a liquid ion exchanger or ion-pair reagent (tertiary or quaternary amine) to further complex the ester molecule. In this process the charge is neutralized. However, only experiments can disclose if the resulting partition coefficient is suitable and within the desired range of $K \approx 3-6$.
2. The “backbone” in the DOTAGA complexing agent molecule is the DOTA molecule with 4 carboxylic groups. Another modified version of this molecule is PCTA (3,6,9,15-Tetraazabicyclo [9.3.1] pentadeca-1(15),11,13-triene-3,6,9-triacetic acid) illustrated in Figure 8. One of the 4 -COOH-groups have been replaced with a non-charged ring system. This molecule is now considered as a possible water/oil partitioning tracer for interwell SOR (PITT) examinations. A modified version of this molecule, in the butyl ester form and complexed with terbium, may look like the illustration in Figure 9. This ester molecule is non-charged and should show a fair degree of oil partitioning. However, it has not yet been synthesized, and must only be regarded as a qualified speculation at this point in time.

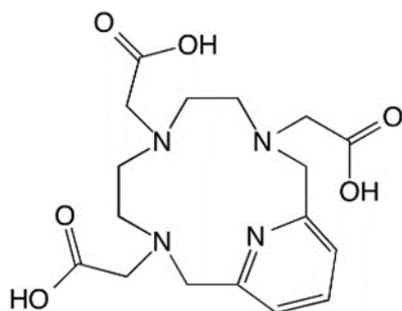


Fig.8. Structure formula of PCTA, a modified version of DOTA.

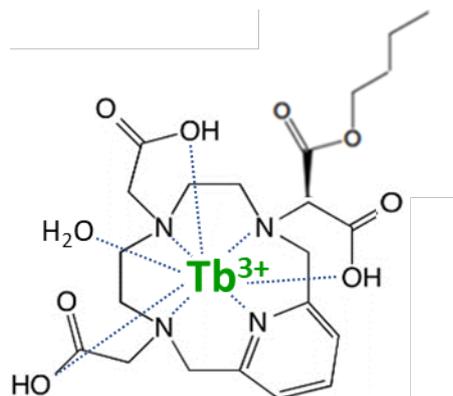


Fig.9. Expected structure formula of PCTA-butyl-ester-Tb

Spin-off

A spin-off of this project is based on the findings that the synthesized and tested DOTAGA-monoethyl-ester-Tb and DOTAGA-monobutyl-ester-Tb molecules offer the possibility to be used as temperature probes in the near-well reservoir formation. This is because of a suitable hydrolysis rate and because they *do not partition* into the oil phase. This possibility has not been further studied and qualified in the present project.

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